periodica polytechnica

Chemical Engineering
51/2 (2007) 57–60
doi: 10.3311/pp.ch.2007-2.09
web: http://www.pp.bme.hu/ch

RESEARCH ARTICLE

Solvent extraction of uranium (VI) by tributyl phosphate/dodecane from nitric acid medium

Moussa Alibrahim / *Habib* Shlewit

Received 2005-10-19

Abstract

Uranium (VI) extraction from nitric acid medium by 20% Tri Butyl Phosphate (TBP)/dodecane was carried out. The effects of the nature of the diluent and nitric acid concentration on uranium distribution ratio (Du) were investigated in this study. The experimental results showed that Du using different diluents increases in the order: chloroform, carbon tetrachloride, dodecane and n-hexane.

The yellow cake [Di-Ammonium Uranyl $U_2O_7(NH_4)_2$] produced at the Uranium Recovery Pilot-Plant from the Syrian row phosphoric acid was used to carry out uranium extraction tests, using 20% TBP/dodecane. Results showed that impurities presented in the yellow cake role as a salting out agent, which explains the increasing of loading capacity of the organic phase.

Infrared studies of $UO_2(NO_3)_2$/20%TBP in dodecane system are reported, uranium was extracted from aqueous solutions of 3 mol/dm^3 HNO_3 containing different Analytical Grade uranyl nitrate concentrations. Infrared spectra of $UO_2(NO_3)_2$.2TBP system indicated that chelation of nitrate to uranyl ion is bidentate. Quantitative analysis of TBP-uranyl nitrate complex in dodecane in the regions of P=O and U=O stretching vibrations is discussed.

Keywords

uranium · extraction · infrared

Acknowledgement

The authors would like to express their thanks to General Director of the Syrian Atomic Energy Commission Prof. I. Othman and the Head of the Chemistry Department for their encouragement to carry out this work. The authors would like to extend their thanks to Ms. S. Alike and Mr. A. Rezkallah for their valuable help to carry out this work.

Moussa Alibrahim

Atomic Energy Commission, Chemistry Department, P.O.Box 6091 Damascus, Syria

e-mail: scientific@aec.org.sy

Habib Shlewit

Atomic Energy Commission, Chemistry Department, P.O.Box 6091 Damascus, Syria

1 Introduction

The purification of crude uranium from its ores at plant-scale using tri butyl phosphate (TBP) started in the early 1950s in Canada and in the UK, then in the US in 1953 [1].

Today, TBP extraction technology and processes are applied word-wide for uranium and thorium purification. Taichi Sato [2] studied the extraction of uranium (VI) from nitric acid solutions using TBP. He found that 6 mol/dm^3 nitric acid was the best concentration for uranium extraction. Moreover, he found that, 97% of uranium can be recovered from 6 mol/dm^3 HNO_3 solution containing less than 0.042 mol/dm^3 uranium using 19%TBP/kerosene. The spectra of organic phases, for the system $UO_2(NO_3)_2$/20%TBP in Dodecane have been interpreted by several investigators, where they concluded that, the P-O-C vibration at 1021 cm^{-1} is not affected by acid and metal content in the organic phase, and the P=O vibration band was shifted to 1191 cm^{-1} due to the coordination of UO_2^{2+} cation as well as, to dimeric nitric acid species [3,4,7]. Literature data investigations of the system M+HNO_3/TBP+ alkane (where M= UO_2^{2+}) highlighted a major role of HNO_3 in the phenomen [3,8]. It has been established that the uranyl ion in various compounds has three vibrational frequencies [5]: a symmetric stretching frequency at 860 - 880 cm^{-1}, an asymmetric stretching frequency at 930 - 960 cm^{-1}, and a bending frequency at 199-210 cm^{-1}. Caldow et al. [6] have quantitatively determined the content of uranium in KBr disk by observation of the symmetric stretching frequency. Borkowski et al. [8] concluded that, when the aliphatic diluents have shorter chain, the solubility of the complex increases and a third phase formation is less likely.

The goal of this work was to investigate the influence of nitric acid concentration, effect of various diluents and the impurities presented in the Syrian yellow cake produced form wet phosphoric acid. Infrared studies of the organic phase TBP/dodecane loaded with $UO_2(NO_3)_2.6H_2O$ were carried out in order to identify the species present and their corresponding infrared bands. Effect of the metal nitrate complexes with TBP has been concerned too.

2 Experimental

2.1 Reagents

Analytical Grade $UO_2(NO_3)_2.6H_2O$, chloroform, carbon tetrachloride, n-hexane, dodecane and salts of $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, NH_4VO_3, $Cu(NO_3)_2.3H_2O$ and $Fe(NO_3)_3.9H_2O$ were obtained from MERCK. Tri butyl phosphate (TBP) was obtained from FLUKA.

2.2 Sample Preparation and Analysis

Organic solutions containing 20% TBP in dodecane, were contacted with equal volumes of 3 mol/dm^3 HNO_3solutions containing progressively increasing uranium (VI) concentrations (15, 25, 35, 45, 55) g/dm^3 (prepared from the analytical grade uranyl nitrate), under the following conditions: 25˚C, mixing time 5 min and phase ratio = 1:1. During this time the equilibrium was usually established. Uranium was determined in the organic phase solutions $[U]_{org}$ by volumetric method, and uranium in the aqueous solutions$[U]_{aq}$ was calculated by mass balance, distribution ratio (D_u) was calculated using the following formula: $D_u=[U]_{org}/[U]_{aq}$. To determine the effect of the acid medium concentration on uranium distribution, solutions of 0.1, 0.5, 1.0, 2.0, 3.0 and 5.0 mol/dm^3 of nitric acid containing 55 g/dm^{3}uranium were prepared and contacted with 20% TBP in dodecane. Organic solutions of 20 % TBP in chloroform, carbon tetrachloride and n-hexane instead of dodecane were contacted with equal volume of 3 mol/dm^3 HNO_3 solutions containing increasing uranium(VI) concentrations (15, 25, 35, 45, 55) g/dm^{3}to investigate the effect of the nature of the diluents on uranium distribution (D_u).

Yellow Cake produced at the Uranium Extraction Pilot Plant from the Syrian raw phosphoric acid, was used to prepare solutions containing 55 g/dm^{3}uranium in 3 mol/dm^3 nitric acid, which were contacted with organic solutions of 20% TBP in dodecane. The infrared spectra of the organic phases were recorded using Fourier Transform Infrared Spectrophotometer (JASCO-300E) with a resolution of 4 cm^{-1} using KRS-5 windows, the cells path lengths for sample and reference were 0.015 mm. Reference cell contained 20% TBP/dodecane pre-equilibrated with 3 mol/dm^3 HNO_3. In order to determine the interference effect of some co-extracted elements (Cu, Ni, Fe, Co and V) on the FTIR spectra, 1 g/dm^{3}of each separately, was added to each of the aqueous solutions of 3 mol/dm^3 nitric acid containing (15, 25, 35, 45, 55) g/ dm^3 uranium and contacted with the organic phases of 20% TBP in dodecane.

3 Results and Discussion

3.1 Extraction of U(VI) from Nitric Acid Solutions

Uranium extraction from aqueous solutions containing uranyl nitrate in nitric acid of 0.1, 0.5, 1, 2, 3 and 5 mol/dm^3 was carried out using 20% TBP/ dodecane. The extraction isotherm curves for the feed solutions containing 55 g/dm^3 uranium are shown in Fig. 1. This indicates that the loading capacity of the organic phase rises considerably with increasing initial concentration of nitric acid up to 3 mol/dm^3.

Yellow cake produced in a pilot plant for uranium extraction from the Syrian wet-phosphoric acid was used to prepare solution of 55 g/ dm^3 uranium in 3 mol/dm^3 HNO_3 and uranium extraction carried out using 20% TBP/ dodecane. Fig. 2 shows uranium extraction isotherm curves from pure uranyl nitrate and yellow cake solutions in 3 mol/dm^3 HNO_3. It can be concluded that the loading capacity of uranium in the organic phase using yellow cake solution is higher, this difference is attributed to the certain impurities in the yellow cake (Table 1), where, impurities here act as salting out agents. Moreover, experimental results showed that using 20% TBP/dodecane is the most convenient concentration, because, the produced uranyl nitrate analyses showed that using higher TBP concentration decreases the selectivity of uranium extraction from yellow cake.

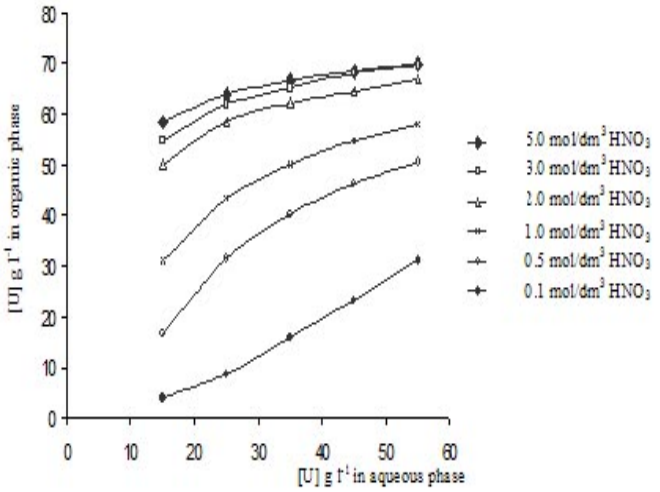

Fig. 1. Uranium extraction isotherm from various nitric acid concentrations using 20% TBP/dodecane.

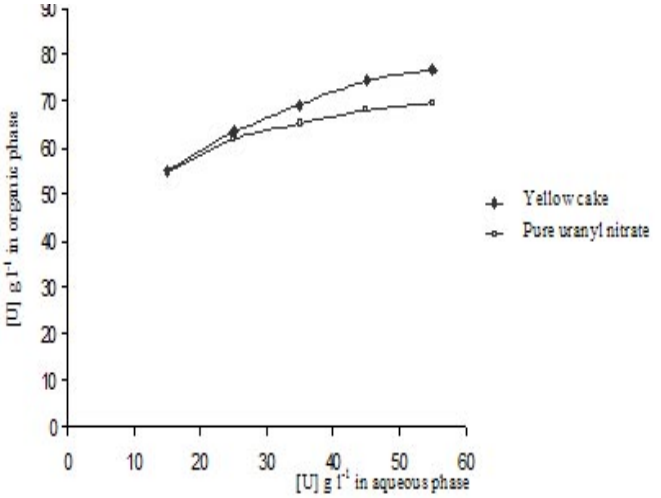

Fig. 2. Uranium extraction isotherm from yellow cake and pure uranyl nitrate in 3 mol/dm^3 nitric acid solutions.

Tab. 1. Some of the Syrian yellow cake contents.

U(%)	Fe(ppm)	Cu(ppm)	Ni(ppm)	V(ppm)	Cd(ppm)
47	950	60	25	21	15

3.2 Effect of Nature of Diluent on the Extraction of Uranium

The extraction of uranium (VI) from 3 mol/dm^3 nitric acid solutions has been studied using 20% TBP in various diluents (Table 2). The results clearly demonstrate that diluents such as hexane and dodecane having low dielectric constants show higher extraction distribution of uranium (VI). On the other hand, lower extraction was observed with diluents having higher dielectric constant such as carbon tetrachloride and chloroform. The difference may be due to the interaction that takes place between the diluent and the extractant, farther, some diluents favour the polymerization of the extractants while others do not. In view of the commercial availability and higher extraction efficiency, in the present studies, dodecane has been chosen as the diluent.

Tab. 2. Influence of the nature of the diluent on uranium extraction distribution D_{U1}, D_{U2}, D_{U3}, D_{U4} and D_{U5} from 3 mol/dm^3 nitric acid solutions containing increasing uranium concentration of 15, 25, 35, 45 and 55 g/ dm^3 respectively.

Diluent	Dielectric Constant	D_{U1}	D_{U2}	D_{U3}	D_{U4}	D_{U5}
Chloroform	4.90	3.21	2.83	2.31	1.84	1.24
Carbon tetrachloride	2.24	7.22	6.74	5.68	4.37	3.91
Dodecane	2.01	12.89	8.33	7.35	7.29	5.41
n-Hexane	1.89	11.93	7.39	6.96	6.87	5.19

3.3 FTIR Measurement

Fig. 3 shows the infrared spectrum of 20%TBP in dodecane system in the range of (600-1600) cm^{-1}. The following regions were found:

1 The phosphoryl region involving P=O stretching vibration, which occurs at 1282 cm^{-1}. This represents coordination of the HNO_3 and metal cations to the oxygen of the P=O group causing a shift of the frequency to lower energy.

2 The P-O-C vibration at 1028 cm^{-1}, which is not affected by acid and metal content in the organic phase.

FTIR spectra of the loaded organic phase solutions, upon U(VI) extraction, which contain (13.92, 22.32, 30,81, 39.57, 46.42) g/dm^3 uranium, are represented in Fig.4 which shows that P=O vibration band of uranium TBP complex, was shifted to 1193 cm^{-1}due to the coordination of UO_2^{2+} cation as well as to dimeric HNO_3 species. The shift of the P=O frequency with respect to the net TBP was about 89 cm^{-1}, and the magnitude of the shift was consistent with those observed for the other uranyl complexes with other organophosphorus ligands and those of other metal ions with TBP [9, 10]. The strong absorption band at

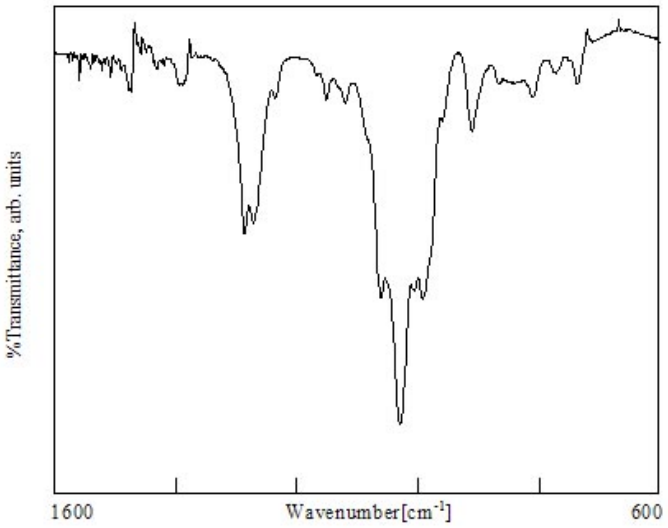

Fig. 3. Infrared spectrum of 20% TBP in dodecane.

940 cm^{-1} led to the suggestion that this band might be used for the identification of uranyl ions. K.W. Bagnall [11] has reported that in the spectra of uranyl nitrate hexahydrate the asymmetric stretching frequency of uranyl ion is observed at 931 cm^{-1}. In this work U=O stretching frequency of $UO_2(NO_3)_2$.2TBP complex is observed at 940 cm^{-1}.

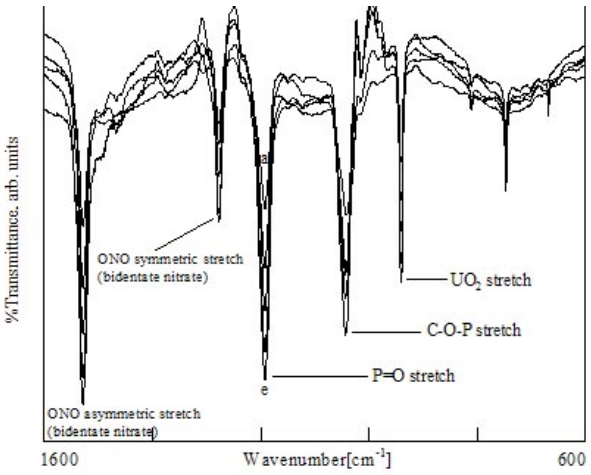

Fig. 4. Infrared spectra of the loaded organic phase solutions. (a: 13.92 g/dm^3; b: 22.32 g/dm^3; c: 30.81 g/dm^3; d: 39.57 g/dm^3; e: 46.42 g/dm^3).

The separation $\Delta\nu$ of the asymmetric ν_1, and symmetric ν_2 of ONO stretching frequencies can be used to determine the mode of the nitrate coordination to the metal [12, 13, 14]. A $\Delta\nu$ larger than 186 cm^{-1} indicates a bidentate chelate environment, while a $\Delta\nu$ at 115 cm^{-1} or lower indicates a monodentate coordination. For all the studied solutions a $\Delta\nu$=251±5 cm^{-1} (ν_1 at 1528 cm^{-1} and ν_2 at 1277 cm^{-1}) was found indicating bidentate chelation of nitrate to uranyl ion. The intense and relatively sharp bands of 1193 cm^{-1} (P=O) and 940 cm^{-1} (U=O) almost not interfered from neighbours, show the possibility of the infrared Spectrophotometric determination of the complex [$UO_2(NO_3)_2$.2TBP] in dodecane. The spectra obtained in Fig. 4 for the complex [$UO_2(NO_3)_2$.2TBP] has been expanded and depicted in Fig. 5 and Fig. 5 for P=O at 1193

cm^{-1} and U=O at 940 cm^{-1} bands respectively. Fig. 5 represents P=O band intensity as a function of uranium concentration and Fig. 6 represents U=O band intensity as a function of the same uranium concentration. The plot of the optical density at P=O and U=O stretching vibration bands against the concentration of $UO_2(NO_3)_2.2TBP$ illustrates that Beer-Lambert law is held for the concentration range used.

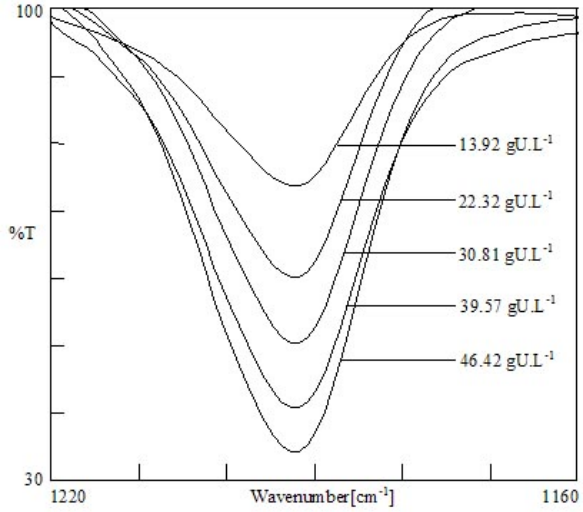

Fig. 5. Changes of the 1193 cm^{-1} band (P=O coordinated with UO_2^{2+}) with increasing concentration of uranium in organic phase.

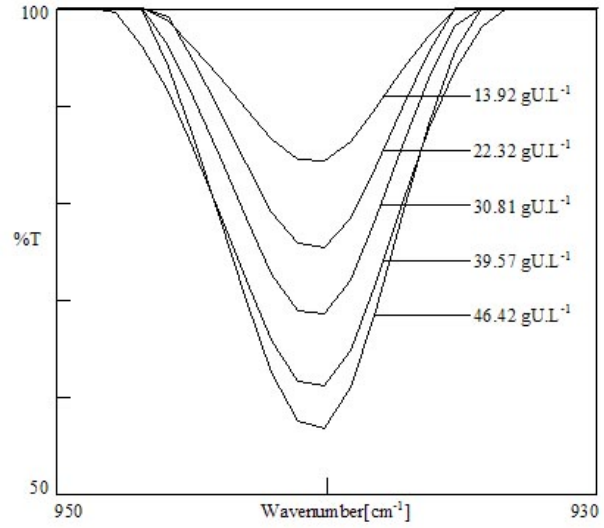

Fig. 6. Changes of the 940 cm^{-1} band (U=O) with increasing concentration of uranium in organic phase.

3.4 Effect of the Co-extracted Elements

Aqueous solutions of 3 mol/dm^3 HNO_3 containing (15, 25, 35, 45, 55) g/dm^3 uranium and 1 g/dm^3 copper, were contacted with 20% TBP/dodecane. Results showed that the peak of P=O vibration band of uranium complex with TBP was interfered by the neighbouring band of copper complex with TBP, and the peak of U=O vibration band of uranium complex with TBP was not interfered by the copper nitrate complex with TBP. The same observations were appearing when Co, Ni and Fe nitrate complex were formed with TBP. Results also showed that oxymetal ions complexes with TBP such as vanadium were interfered with the P=O and U=O vibration bands. These observations indicate the possibility of the infrared spectrophotometric determination of $UO_2(NO_3)_2.2TBP$ in organic solvents, in the region of U=O vibration bands in all cases, except for the presence of metal nitrate containing the oxymetal ions.

4 Conclusion

Uranium extraction isotherm curves indicate that, the extraction distribution ratio of uranium from nitric acid medium by 20% TBP/dodecane increases as the nitric acid concentration increases up to 3 mol/dm^3. Impurities in yellow cake, role as salting out agents and improve uranium extraction distribution. Results show that uranium extraction distribution increases as the dielectric constant of diluent decreases. Infrared spectra of $UO_2(NO_3)_2.2TBP$ system, indicated that chelation of nitrate to uranyl ion is bidentate. Intense and relatively sharp bands of P=O and U=O showed the possibility of the infrared spectrophotometric determination of the complex $UO_2(NO_3)_2.2TBP$ in dodecane in all cases, except for the presence of metal nitrate containing the oxymetal ions.

References

1 **Schulz WW, Navratil JD, Bess T**, *Science and Technology of Tributyl Phosphate*, Selected Technical and Industrial uses, Part A. Florida **II** (1987).
2 **Sato T**, J. Inorg. Nucl. Chem. **6** (1958), 344.
3 **Ferraro JR, Borkowski M, Chiarizia R, McAlister DR**, J. Solvent Extraction and Ion Exchange **19** (2001), no. 6, 981-992.
4 **Ohwada K, Ishihara T**, J. Inorg. Nucl. Chem. **28** (1966), 2343–2345.
5 **Conn GKT, Wu CK**, Trans. Faraday. Soc. **34** (1938), 1483.
6 **Caldow GL, Van Cleave A.B, Eager R.L.**, Can. J. Chem. **38** (1960), 772.
7 **Chiarizia R, Jensen M.P, Borkowski M, Ferraro JR, Thiyagarajan P, Littrell KC**, J. Solvent Extraction and Ion Exchange **21** (2003), no. 1, 1-27.
8 **Borkowski M, Ferraro JR, Chiarizia R, McAlister DR**, J. Solvent Extraction and Ion Exchange **20** (2002), no. 3, 313-330.
9 **Burger LL**, *Physical properties*, Science and Technology of Tributyl phosphate (Schulz WW, Navratil JD, eds.), CRC Press: Boca Raton, Florida, 1984, pp. 26-62.
10 **Peppard D.F, Ferraro JR**, J. Inorg. Nucl. Chem. **10** (1959), 275-288.
11 **Bagnall KW, Wakerley MW**, J. Inorg. Nucl. Chem. **37** (1975), 329-330.
12 **Gatehouse B.M, Livingstone S.E, Nyholm R.S.**, Chem. Soc. (1959), 4222–4225.
13 **Curtis N.F, Curtis Y.M.**, J. Inorg. Chem. **4** (1965), 804-809.
14 **Ferraro J.R, Peppard DF**, Nucl. Science Eng. **16** (1963), 389-400.